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PHYSICAL-CHEMICAL AND TECHNOLOGICAL FACTORS IN COLORING MOLTEN GLASS

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The main conditions for colorants to dissolve in glass melts — chemical interaction, diffusion, distribution in bulk or in a definite layer — are examined. The particularities of continuous volume and surface coloring of glass in container- and sheet-glass production are noted, and the corresponding dependences are presented.

Key words: coloring, chemical interaction, diffusion, mixing, residence time, glass container, sheet glass.

Coloring molten glass is a complex process in glass technology. It is involves a chemical interaction, transport and uniformity of the distribution of the coloring complexes in the bulk or a definite layer. The transfer and uniformity of the distribution of different liquid media is one of the main characteristics of mixing. The phenomena and processes involved in the mixing of liquids are pervasive in nature and technology during the movement of water in natural reservoirs and in technological industrial processes in the production of metals, glass, ceramics, polymers and so forth.

In glass production, mixing processes conducted in melts in order to increase their uniformity occur at the manufacturing stages of glassmaking and preparation of the molten glass for pouring. In continuous tank furnaces difficulties arise when it is necessary to switch from one color to another in order to color the glass. The color in molten glass can be changed directly in a furnace in two ways:

- 1) pouring the molten glass out completely and making molten glass with the required color;
- 2) gradually transitioning to glass of a different color while the furnace is in operation.

In the first case significant losses of molten glass and therefore raw materials are unavoidable, and fuel is not used efficiently. In addition, no product is produced for a definite period of time, so that the performance of the furnace and the installed equipment decreases, which increases the production costs. In the second case the process of transitioning to making glass with the required color takes a long time, and

the customer may not be satisfied with the intermediate color tones. Thus, neither variant for changing the color of the molten glass is desirable the standpoint of technology or economics, especially when the change must be made quickly and repeatedly. The basic principles of manufacturing are not satisfied in this process [1].

Coloring and in-line color chance can be effectuated by making special technological and structural changes after the glassmaking stages have been completed. In mechanized production of glass and glass articles colorless glass can be colored as follows:

- 1) prior to mechanized formation of hollow blown and pressed articles (volume coloring); because the coloring and change of color of molten glass must be done in a continuous flow the feeder channel is lengthened and equipped with additional mixing facilities and devices (electric heating, bubbling, thresholds, mixers and so on) [2, 3];
- 2) after sheet glass is formed in the float process (surface coloring); coloring is done by an electrochemical method using special apparatus and low-melting metals and alloys [4, 5].

We shall examine the factors affecting colorant dissolution in melts: the chemical interaction of solid colorants with melts, diffusion, particularities of coloring colorless molten glass in a continuous flow during the manufacture of glass containers and sheet glass.

Chemical Interactions. During the making of colored glass the colorants initially react with Na₂CO₃ melt (fast interaction) and subsequently with the glass-forming melt (slow interaction). Because the melting temperature of

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Colorant	Atomization energy, kJ/mole [6]	50% dissolution time at 1200°C, min	Dissolution activation energy, kJ/mole
Co ₂ O ₃ (CoO)	914.6	2.4	107.3
NiO	914.18	2.5	107.3
MnO_2	1300.0	3.9	147.6
Fe_2O_3	2410.6	4.9	182.7
Cr ₂ O ₃	2680.7	6.2	242.2

TABLE 1. Characteristics of Colorant Interaction with Na₂CO₃ Melt

Na₂CO₃ is relatively low (854°C) melt appears early and reacts strong with the components of the batch, including the colorants. In this connection the character of the colorant—melt interaction was studied.

The results of an analysis of the reference and experimental data are summarized in Table 1.

The data in Table 1 show a definite correlation between the activation energy of atomization, the dissolution rate and the activation energy of the process. Colorants with the strongest crystal lattice dissolve more slowly.

Analysis of the experimental data shows that the colorant dissolution process is comprised of surface and volume components [7, 8]. The surface component characterizes the interaction at the interface and the volume component characterizes the removal of the interaction products into the interior of the melt and the formation of the final melt with a definite composition.

Analysis of the temperature dependence of the parameters characterizing the surface and volume components shows the presence of adsorption phenomena in the interaction. This suggests a mechanism for the interaction of Na₂CO₃ melt with colorants for the case of Cr₂O₃.

1. Attack on the Cr₂O₃ crystal lattice by Na⁺ ions in the melt, chemisorption and formation of active surface complexes:

$$O = Cr - O - Cr = O + 2Na^{+} ... CO_{3}^{2-} \rightarrow O = Cr - O - Cr = O (2Na^{+} ... CO_{3}^{2-})_{ads}$$

2. Breaking of bonds with the Cr₂O₃ crystal lattice and formation of surface radicals:

$$O = Cr - O - Cr = O \rightarrow O = Cr - O - + - Cr = O$$
.

3. Interaction of surface radicals with adsorbed structural units of the melt:

$$O = Cr - O - Na - O$$

+ $C = O \rightarrow 2(O = Cr - O^{-}Na^{+}) + O = C = O$

Partial interaction of the surface compounds with excess melt and oxygen with the formation of the complexes Cr⁶⁺ occurs.

4. Detachment of structural groups and blocks from the surface, their transport in the interior of the melt and formation of coloring complexes.

Colored glasses can be regarded as solutions of complex compounds of transition and rare-earth metals in a glassy medium, and in this connection the interactions occurring in the coloring complex—glassy solvent system play an important role. Such interactions are described in detail in the theoretical principles of inorganic chemistry [9], but such research remains virtually undeveloped for glasses.

Three kinds of oxygen ions, which are in equilibrium, exist in glass melts as a result of the chemical reactions and thermal and electrolytic dissociation. Their ratio is determined by the law of mass action; the concentration dependence of the equilibrium constants can be expressed by the equation

$$K = \frac{[O^0][O^{2-}]}{[O^-]}.$$

Using the law of mass action, G. Tup and S. Samis analyzed these equilibria (1962). The results are generalized in [10].

The three kinds of oxygen ions have very different chemical properties. The O^{2-} ion acts as a reducer (it gives up electrons) while O^{-} as an oxidizer (it accepts electrons). The bridge ion O^{0} , being covalently bound with the silicon ions, is relatively inactive. The fact that the oxygen ions play different roles in an oxidation-reduction interaction with chromium ions can be shown by the equation (the electronic configuration of the ions is presented in parentheses):

$$Cr^{6+}(3d^0) + O^{2-}(2p^6) \leftrightarrow Cr^{3+}(3d^3) + O^{-}(2p^5).$$

The composition of glass has a large effect on the colorant dissolution in molten glass. This effect was studied by the rotating disk method, which makes it possible to perform experiments under definite controllable conditions in accordance with the hydrodynamic laws governing the motion of a liquid (glass melt) [11]. The composition of commercial container glass was taken as the base and Cr₂O₃ as the colorant. The composition was changed by replacing SiO₂ with a corresponding oxide. The temperature of the experiments was 1500°C. The results are presented in Fig. 1. It is evident from the figure that Na₂O increases the dissolution rate of the colorants the most. CaO also increases the dissolution rate but less than Na₂O. The effect of MgO is negligible. Al₂O₃ decreases the dissolution rate of colorants. The results obtained can be attributed to the effect of the oxides studied on the viscosity.

Diffusion. Diffusion phenomena play a large role in the dissolution of colorants in glass melts. At the same time there is not enough information on the real values of colorant dis-

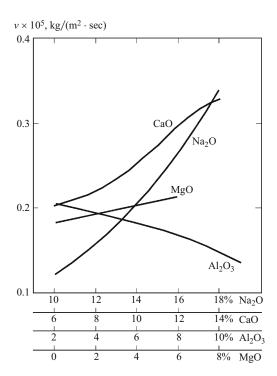


Fig. 1. Effect of glass composition on the dissolution rate of Cr₂O₃.

solution rates and diffusion coefficients in glass melts. The rotating disk method makes it possible to determine and compare these characteristics [12]. The diffusion coefficient was determined from the equation

$$v = 0.62D^{2/3}v^{-1/6}(C_s - C_\tau)\sqrt{\omega},$$
 (1)

where v is the rate of dissolution of the sample, D is the diffusion coefficient, v is the kinematic viscosity, C_s and C_τ are, respectively, the saturation and running concentrations and ω is the angular velocity of the sample.

The data on the properties of the glass, the concentration ratios and the computational results for the diffusion coefficient obtained using Eq. (1) are summarized in Table 2.

Analysis of the experimental data showed that the temperature dependence of the dissolution rate can be described by the equation

$$\log \frac{v}{\sqrt{\omega}} = a - \frac{b}{T},\tag{2}$$

where a and b are coefficients.

A similar equation describes the temperature dependence of the diffusion coefficient. The temperature dependences of the Cr_2O_3 dissolution rate and diffusion coefficient are presented in Fig. 2. The activation energies of the dissolution and diffusion processes were determined from the experimental data; the values are 250 and 326 kJ/mole, respectively. Thus, the experimental results show that diffusion transport governs Cr_2O_3 dissolution.

TABLE 2. Calculation of the Diffusion Coefficients D at Different Temperatures

<i>T</i> , K	Density, 10 ³ kg/m ³	$10^{-2} \text{m}^2/\text{sec}$	$(C_{\rm s} - C_{\rm \tau}),^* {\rm kg/m^3}$	D , $10^{-11} \text{ m}^2/\text{sec}$
1623	2.32	1.14	28.4	1.26
1673	2.30	0.93	19.5	2.24
1723	2.28	0.71	17.2	4.17

^{*} For $v/\sqrt{\omega} = 2 \times 10^{-7}$.

Coloring as a Mixing Process. The technological difficulties arising when the color of the glass must be changed in a continuous tank furnace were noted above. In this connection an in-line color change is best effectuated in a special feeder located next to the tank, where the colorless molten glass is obtained, in a glassmaking furnace. The character of the dissolution and the colorant distribution in glass melts depends on the temperature, the type of colorant and its method of introduction and the condition of mixing. The effect of the temperature is expressed in the change in the conditions for transport phenomena (as temperature increases the viscosity decreases and molten glass flows and diffusion processes are activated). It is necessary to take account of the rates of interaction of different colorants with the melt, for example, selenium dissolves in melt much more rapidly than Cr₂O₃. Finally, mixing, which activates diffusion and distribution processes, makes it possible to obtain uniform coloring of the melt.

It should be noted that the use of colorants in different forms makes it possible to single out two cases on the basis of the character of their interaction with the main melt:

- interaction in the melt solid (colorant powder) system;
- interaction in the melt melt (frits) system.

When particles of a solid colorant are introduced into the molten glass and the melt is mixed a "viscous" regime where the diameter of the dissolving particles is much shorter than the distance over which the local flow velocity changes appreciably arises [13]. In this case the finely dispersed colorant particles follow the melt flows almost completely and the efficiency of the diffusion transport is low. When coloring frits (low-melting glass with a high colorant content) are used the two melts in the system interact with one another and the mixing efficiency increases considerably as a result of an increase of the interaction surface. Similar conditions are also created with granular colorants, when a colorant initially dissolves in the active component (for example, Na₂CO₃) and then the interaction occurs in a system of two melts.

As noted above, for high-viscosity glass melts it is practically impossible to create a developed turbulence regime. In this connection a series of studies was devoted to conditions of laminar (mechanical) mixing, in which the role of diffusion is negligible.

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Extensive theoretical, experimental and practical data are now available on mixing processes including for viscous liquids, characterized by laminar mixing. In one of the first works on the construction of a scientific foundation of the process of mixing of two liquids whose properties are different (for example, the density, viscosity or color are different), C. Eckart proposed that three stages of the process be singled out:

- initial stage, at which the volumes of both liquids are clearly distinguishable by color; a sharp gradient is present at the boundary between the two liquids, while virtually no such gradient is present inside each liquid; the color gradient averaged over the entire volume is very small and this state can persist for a long time if the two liquids remain stationary;
- intermediate stage, arising when the liquids move and the shapes of their volumes change — they stretch and bend; the boundary surface with a large gradient increases sharply and therefore the color gradient averaged over the entire volume increases;
- *final* stage at which the gradients vanish and the liquid becomes uniformly colored.

The comparatively long duration of the first stage is due to the slowness of diffusion or heat conduction processes. At the third stage vanishing of the gradients is predominantly due to molecular diffusion "prepared" at the second stage. The author proposed that the physical process of mixing be classified according to the criterion of whether or not the diffusion is taken into account. For processes where diffusion can be neglected (for example, for processes that are not prolonged compared with the typical diffusion time for the given liquids), he introduced the term "mechanical mixing" (stirring) in contrast to "molecular mixing" (mixing) taking diffusion into account.

In [15] previous studies are analyzed and a methodology is developed for studying, mathematical modeling and optimizing two-dimensional laminar mixing.

It should be noted that the particularities of mixing liquids, indicated above, are present in a melt of colorless glass interacting with a coloring melt.

Kinetic Relations for Continuous Coloring of Molten Glass. The coloring of molten glass in a continuous flow is an example of continuous processes where the uniformity of mixing of colorless molten glass with a coloring melt plays the main role. It should be noted that mixing processes have been studied in greatest detail for the processes and apparatus used in chemical technology [16, 17]. But the fundamentals of mixing processes are fully applicable to the processes used in glass technology, specifically, homogenization and volume coloring of a glass melt.

In apparatus with mixers, for two liquid media the following phenomena associated with mixing can be singled out:

- deformation (predominantly stretching and bending)
 of layers accompanying an enlargement of the interface;
- movement of groups of particles from one position into another convective mixing;

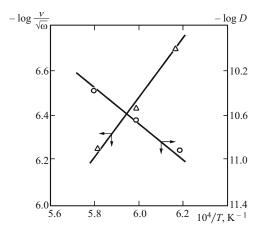


Fig. 2. Temperature dependences of the ${\rm Cr_2O_3}$ dissolution rate and diffusion coefficient.

 change in the position of the individual particles of a layer — diffusion mixing.

Coverage of the entire cross section of the melt by the mixers with a change of flow direction increases the role of the phenomena enumerated above, especially those associated with deformation. This was confirmed by experiments with different types and variants of mixing elements.

If a liquid requiring homogenization flows continuously through the apparatus, the following cases can occur in this apparatus depending on the mixing intensity:

- 1) ideal displacement;
- 2) ideal (complete) mixing;
- 3) incomplete (partial) mixing.

In the first case the particles of liquid enter and leave the apparatus without mixing with one another. The residence time of each particle in the apparatus is the same and equals the time required for the flow to pass through the apparatus. In reality flows of this type do not arise in Newtonian liquids, including glass melts, because of the presence of molecular (ionic) diffusion. In the case of ideal (complete) mixing the residence time of individual particles of liquid in the apparatus is different and varies from 0 to ∞ . This process is also idealized. In reality it does not occur; it is realized only in some approximation. In practice, only the third case need be considered.

In a continuous apparatus, the distribution of the residence time of individual particles of liquid is of interest for mixing and homogenizing any liquids. Fundamental research in this field has been done by P. Dankwerts [18, 19]; this work has been elaborated in the mathematical modeling of continuous dissolution processes [20].

The following relation holds for continuous apparatus:

$$\tau'' = V/w, \tag{3}$$

where τ'' is the average residence time of the particles in the flow apparatus, V is the volume of the apparatus and w is the flow rate of the liquid.

This relation also holds for colored particles. The longer the average residence time of the colored particles in the apparatus, the greater the homogenization and color uniformity are.

At the same time the relation (3) represents the time required for complete exchange of the liquid in the apparatus. In this connection it is convenient to represent the coloring kinetics of molten glass in a continuous flow as a function of time, expressed as fractions of the average residence time or the total exchange time.

In accordance with the data of [17, 18], the following expression is valid for ideal mixing kinetics:

$$c_{\rm rel} = 1 - e^{-\tau/\tau''},$$
 (4)

where $c_{\rm rel}$ is the relative concentration, i.e., the concentration at a given moment in time expressed as a fraction of the prescribed concentration, $c_{\rm rel} = c_{\tau}/c$; τ is the running time; and, τ'' is the average residence time.

For ideal mixing, at $\tau = \tau''$ $c_{\rm rel} = 1 - 1/e = 0.632$. This means that only 63.2% of the particles reside in the apparatus for a time shorter than the residence time. As $\tau \to \infty$ $c_{\rm rel} \to 1$, i.e., the running concentration will go to the prescribed value.

Under the actual conditions of coloring of molten glass in a continuous flow the kinetics of coloring will differ from that of ideal mixing. The character of this difference can be evaluated by comparing the kinetic curves of coloring with the ideal mixing curve constructed for prescribed conditions of coloring.

The kinetic curves of the coloring of molten glass in rose and green colors by granular colorants with the prescribed concentration 0.05% (Se, Cr₂O₃) are presented in Fig. 3. The data were obtained by using a coloring feeder with electrothermal and mechanical mixing zones. The curves of ideal mixing and ideal displacement are presented for comparison. Significant differences of the kinetic coloring regimes from ideal mixing are evident in Fig. 3. The magnitude of this difference can be evaluated according to the area between the ideal mixing curve and the corresponding kinetic curve. At the same time elements characteristic for ideal displacement are also present in a real coloring process.

In summary, the kinetic curve of coloring can be divided approximately into to two sections — mixing and displacement sections. The point of intersection of the kinetic curve of coloring and the ideal mixing curve can serve as the point of separation of these sections.

As follows from Fig. 3, for the coloring of molten glass in a continuous flow the deviations from the ideal mixing regime are quite large. For identical mixing conditions this is due to the high viscosity of the molten glass and the character of the colorant.

The kinetic curves presented in Fig. 3 were obtained with molten glass output 50 kg/h, electric heating, three mixing elements with rotation rate 18 rpm and colorant feeding

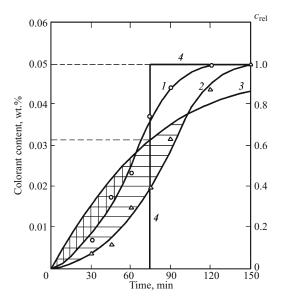


Fig. 3. Kinetic curves of the colorant content in molten glass: *1*) Se coloring; *2*) Cr₂O₃ coloring; *3*) ideal mixing curve; *4*) ideal displacement curve.

25 g/h. It should be noted that selenium coloring of the molten glass occurs quite easily and a mixing regime change has no special effect on the coloring kinetics. For chromium colorants the coloring process slows down and the coloring uniformity depends strongly on the mixing regime. Chromium compounds are not assimilated by the molten glass as easily as selenium; this is due to the chemical nature of the colorant and the smaller diffusion coefficient. This is also expressed in the fact that for low mixing intensity and powdered colorants the prescribed $\rm Cr_2O_3$ concentration in the glass usually is not attained and "black spots" (undissolved $\rm Cr_2O_3$ particles) appear in the molten glass.

Continuous Volume Coloring in Glass Container Production. Glass container production is characterized by high molten glass output. In this connection, the use of physical-chemical (granulation or fritting of colorants) and mechanical (active mixing of the melt) factors is mandatory. Ordinarily, coloring frits (low-melting glass with low surface tension and high colorant content), which can be delivered in the form powder or melt to the surface of the molten glass using appropriate feeding apparatus, are used. The mixing systems must create a complex motion of the molten glass in the vertical and horizontal directions. The surface activity of the coloring frits with respect to the colorless molten glass with the basic composition promotes good mixing.

Diagrams of the feeder channel and the direction of motion of the flows in the mixing zone with continuous coloring of the molten glass in the production of small glass articles are shown in Fig. 4. Propeller mixers placed at the walls of the feeder channel (the mixers create downward radial-axial circulation of the molten glass) and three rows of screw mixers (these mixers create predominantly upward axial circulation) are used for mixing. A complex motion of the molten

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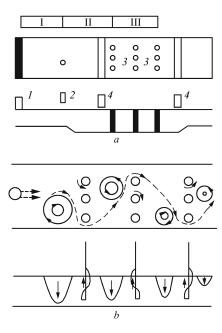


Fig. 4. Technological scheme of a channel for continuous coloring of molten glass (a) and the motion of the molten glass during coloring (b): I) pre-heating zone; II) feed zone and initial colorant distribution; III) mixing zone; I) foam clearing bar; 2) colorant feed tube; 3) mixers; 4) gates regulating the regimes in the gas space of the mixing zone.

glass in the horizontal direction (one of the trajectories of motion is shown) and the vertical direction is observed in the feeder channel. Together with radial-axial downward circulation the propeller mixers direct the molten glass flow from wall to wall at the same time. Sections with circular motion, slow and fast flows, are present. For example, slow flow from the left-hand side of the channel and fast flow from the right-hand side are created on the section of the first row of mixers. Subsequently, color uniformity is obtained by alternation of the velocities along the sides of the channel and using low-melting frits. As the molten glass output increases the number of rows of mixers increases.

Continuous Electrochemical Surface Coloring of Sheet Glass. Electrochemical surface coloring of polished sheet glass, obtained by floating molten glass on a bed of molten tin, is another continuous method of coloring. Low-melting metals and alloys are used for electrochemical coloring of glass. The coloring melt must wet the holder electrode well and not wet the glass ribbon. When an alloy consisting of 98 - 99% lead and 1 - 2% copper is used the holder electrode is made of copper. In this case the tin melt is the cathode, the lead-copper melt is the anode and the glass ribbon is the electrolyte. The holder electrode keeps the lead-copper melt in constant contact with the glass ribbon over its entire width. When the glass ribbon comes into contact from above with the melt of coloring metal, held by the holder electrode, and from below with the tin melt and with a constant voltage from an appropriate source an electrochemical cell is formed.

Under the action of an electric field on the anode–glass interface the lead and copper atoms ionize:

$$Pb^{o} \rightarrow Pb^{2+} + 2e$$
; $Cu^{o} \rightarrow Cu^{+} + e$.

Next, the lead and copper ions undergo electro-diffusion into the glass while the sodium and hydrogen ions electro-diffuse into the tin. In this case the ion flux density J is determined in a general form by the ion concentration C, the ion mobility U and the driving force f of the flow (Theorell's relation):

$$J = C U f. (5)$$

In accordance with the laws of thermodynamics of irreversible processes the driving force of the flow is equal to the gradient of the electrochemical potential in the direction of the flow with opposite sign: $f = -d\mu/dx$. Subsequent transformations lead to the Nernst–Planck equation

$$J = -\left(D\frac{\mathrm{d}C}{\mathrm{d}x} + CUzF\frac{\mathrm{d}\varphi}{\mathrm{d}x}\right),\tag{6}$$

where J is the ion flux density, D the diffusion coefficient, C the ion concentration, U the ion mobility (U = D/kT), k Boltzmann's constant, T the absolute temperature, z the ion charge, F Faraday's number and φ the electric potential.

It follows from the Nernst–Planck equation (6) that the total ion flux (electrodiffusion) in an electric field is the algebraic sum of the diffusion (in the presence of a concentration gradient) and electrophoretic (in the presence of a potential gradient) flows. The combined effect of the concentration and electric gradients in the presence of electrodiffusion is to accelerate ion transport processes, which is especially important for high-viscosity melts and, specifically, for surface coloring of sheet float glass.

As a result of the high viscosity of the glass and the brief contact of the glass with the coloring melt the penetration of lead and copper into the glass is limited by a thin surface layer. After the glass ribbon emerges from the electrochemical contact zone the hydrogen of the protective atmosphere diffuses into the glass and ionizes

$$1.5H_2 \rightarrow 3H^+ + 3e$$

and the lead and copper ions are reduced

$$Pb^{2+} + 2e + 2H^{+} \rightarrow Pb^{0} + 2H^{+}; \quad Cu^{+} + e + H^{+} \rightarrow Cu^{0} + H^{+}.$$

In the process metal nanoparticles and nanoclusters are formed and self-organization and self-assembly of kinetic units occur with formation of colloidal coloring centers [21]. The colored layer of glass is up to 2 μm thick, and most of the 0.04 μm metal particles are concentrated in a 1 μm thick. The coloring process occurs at tin temperature about 1000°C and glass temperature 700 – 800°C. The reduced metal layer directly on the surface of the glass and at depth to about

 $1~\mu m$ evaporates; the surface microlayer of colorless glass with low content of alkali ions fulfills in this case a protective function, increasing the serviceability of the colored sheet glass.

The diffusion processes leading to the formation of a near-surface colloidal-colored layer of glass are due to the rms displacements of the particles in time. In this connection the data in [4, 5, 22] make it possible to obtain ballpark values of the electrodiffusion coefficient of the metal ions in the colloidal coloring of sheet glass, using the relation

$$x^2 \approx 4D_{\rm e}\,\tau,\tag{7}$$

where x is the diffusion penetration depth of the metal ions in the glass, $D_{\rm e}$ the electrodiffusion coefficient and τ the contact time of the coloring metal melt with the glass.

For $x \sim 2 \times 10^{-6}$ m we have $\tau \sim 1$ sec and $D_{\rm e} \sim 10^{-12}$ m²/sec.

There are a number of prescriptions for the coloring alloys. An alloy of cobalt with bismuth is used to obtain glass with a light blue layer near the surface, and cobalt is used for the holder electrode. The rose hue is obtained with alloy of copper and tin, a grayish hue is obtained with an alloy of silver with lead, and so forth. Corresponding technological and electric regimes are used for each type of coloring.

Continuous volume and surface glass coloring processes are complex and have particularities associated with the high viscosity of glass melts. Moreover, the volume coloring processes are similar to homogenization processes occurring during glassmaking. A thorough study of the particularities of coloring will make it possible to improve existing and develop new effective methods for improving glass making and coloring.

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